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(54) Title: BONDED FIBROUS SHEET MATERIAL

(57) Abstract

A porous bonded fibrous sheet material comprises a porous fibrous substrate and a bonding system which is the product obtained by cross-linking a non-film forming coating composition containing a polymer latex and a wet-strength resin. The bonded sheet material is particularly suitable for conversion into food casings (e.g. sausage skins) by a subsequent viscose treatment. Further uses include manufacture of beverage filtration products.

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# BONDED FIBROUS SHEET MATERIAL

The present invention relates to a bonded fibrous sheet material which is useful, for example, in the manufacture of casings (e.g. skins) for food products.

It is well known that a number of food products (particularly certain meat products) are, during their process of manufacture, enclosed within a skin which retains the form or shape of the product. Examples of such food products are sausages, salami etc.

One method which has been used extensively for producing such casings involves viscose treatment of a porous paper web, as described more fully in U.S. Patent No. 3 135 613. Briefly this process involves the steps of

- (1) forming a bonded fibrous web by treatment of the paper with a dilute viscous solution (to apply approximately 1-3% of viscose based on the weight of the paper), drying the web, regenerating cellulose by acid treatment, washing and further drying. The product of this step is a porous, bonded fibrous web having sufficient caustic resistance to withstand the highly alkaline conditions of step (2). Conventionally step (1) has been carried out by the manufacturer of the paper; and
- (2) treating the bonded web obtained from step (1) with a highly caustic viscose solution (to apply 300%-400% of viscose by weight of the paper), followed by regeneration of cellulose and washing and drying steps to produce the food casing material.

The product of step (2) has properties rendering it highly desirable for use as a food casing. More particularly, the casings are:

1. porous and permeable to moisture vapour and smoke thus allowing food products enclosed therein to be processed;
2. dimensionally stable to allow food products which may for example be salami of substantial lengths and relatively heavy to be hung without losing their shape; and
3. clear to the extent that the fibrous base cannot be seen.

Such casings are perfectly satisfactory and have been used for many years. However step (1) does have processing disadvantages in that it is a multi-stage process involving dope addition, acidification, neutralisation and washing stages. The multi-stage process associated with step (2) is an accepted process requirement in the industry and is not seen as a particular disadvantage.

Various patents have discussed the use of alternative materials for bonding paper webs to provide an appropriate substrate for casing forming operations where treatment with concentrated viscose solution under highly alkaline conditions is carried out. After undergoing bonding the substrate must retain its porous, absorbent characteristics in order to permit adequate impregnation and encasement by the converted viscose. The bonding agent should also be one that will not cause the substrate to become discoloured during exposure to the conditions of the casing forming process.

U.S. Patent No. 3,484,256 (Chiu et al) suggests cationic thermosetting resin and polyacrylamide as a replacement for the dilute viscose bonding treatment. U.S. Patent Nos. 3,640,734-5 (Conway), and 3,679,437 (Oppenheimer et al) teach the use of soluble poly (vinyl alcohol) as a wet strengthening agent.

The aforementioned binder materials, whether used alone or in combination frequently provide some but not all of the desired characteristics of the casing. For example the use of poly (vinyl alcohol) having a degree of hydrolysis of about 85% will provide low to moderate dry tensile strengths but poor wet tensile, caustic strength and absorption characteristics. Conversely, the use of fibrous film forming materials such as hydroxyethyl cellulose in conjunction with appropriate cross linking agent such as dialdehyde cross linkers will have the opposite effect from that achieved by the poly(vinyl alcohol). They exhibit good wet tensile strengths and absorbency characteristics but poor caustic tensile strength. Unfortunately, mixtures of these materials also fail to provide all the desired characteristics.

It is therefore an object of the present invention to provide a new and improved binder system capable of imparting the characteristics associated with dilute viscose bonded materials. According to a first aspect of the present invention there is

provided a porous bonded fibrous sheet material comprising a porous fibrous substrate and a bonding system which is the product obtained by cross-linking a non-film forming coating composition containing a polymer latex and a wet-strength resin.

Preferably the amount of the cross-linked composition is less than 40% (e.g. 5 to 40%) by weight of the weight of the untreated substrate. More preferably the amount of the cross-linked composition is less than 20% on the same weight basis. Ideally the amount of the cross-linked composition is in the range 7.0 to 15% by weight with best results usually being obtained in the range 7.5-10% by weight.

According to a second aspect of the present invention there is provided a method of producing a porous bonded fibrous sheet material comprising treating a porous fibrous substrate with a coating composition which under the conditions of the treatment does not form a film and which is an admixture of a polymer latex and a wet strength resin, and effecting cross-linking of the polymer and resin applied to the substrate to produce a porous bonded fibrous sheet material.

In the food casing precursor material of the invention, the cross-linked composition derived from a latex and a wet-strength resin replaces the viscose pre-treatment of the prior art. The food casing precursor material of this invention may be converted to the final casing material by a viscose treatment as employed in the prior art conversions of viscose pre-treated paper or any other suitable material.

Therefore according to a third aspect of the present invention there is provided a food casing material which comprises the bonded fibrous sheet material in accordance with the first aspect of the invention treated with viscose.

Food casing materials produced in accordance with the invention meet requirements 1-3 above. Furthermore the bonding which is achieved between the viscose and the cross-linked coating composition results in lower levels of stress line fracture normally associated with resin bonded casing substrates. Additionally the food casing materials have improved clarity compared to other resin bonded systems and comparable to the clarity of materials obtained using viscose pre-treated substrates.

According to a fourth aspect of the present invention there is provided a food product (e.g. a meat product such as a sausage or salami) enclosed within a food casing material in accordance with the third aspect of the invention.

In addition to its use in the manufacture of food casing materials, the bonded web material of the invention may be used in the production of beverage filtration products, e.g. tea bags, coffee bags etc. The material is also useful in the production of sachets for washing powders and double sided adhesive tapes.

Preferably the porous substrate is a wet laid fibrous substrate, most preferably a paper. Most preferably the paper is of a high and uniform permeability (preferably  $100-200 \text{ m}^3 \text{ min}^{-1} \text{ m}^{-2}$ ) and of low basis weight (typically  $10-30 \text{ gsm}$ ). Preferably also the paper has a tensile ratio (i.e. ratio of machine direction:cross direction strength) of  $0.5-2.0$  more preferably in the range  $1.0-1.5$ . The paper is ideally prepared from "long" fibres (e.g.  $5 \text{ mm}$ ) of high aspect ratio (e.g.  $300-3000$ ). The web's constituent fibres should also exhibit uniform formation and absorbency characteristics. Particularly suitable papers are composed of natural cellulosic fibres typically of the Musa Textilis species (e.g. Abaca). It is also possible to use papers comprised wholly or partially of synthetic fibres.

In the first step of the treatment process, the porous substrate (e.g. paper) is treated with a coating composition which (under the conditions of treatment) is non-film forming to ensure that the precursor material ultimately obtained is porous. The coating composition is an admixture of a polymer latex and a wet strength resin.

The latex is preferably a dispersion of a polymer which is self cross-linkable, typically one for which cross-linking is initiated by removal of water.

The latex is most preferably a dispersion of a copolymer of an olefin and an unsaturated ester. The olefin may for example be an  $\alpha$ -olefin having 2 to 8 (preferably 2 to 4) carbon atoms and the unsaturated ester may be a vinyl ester, preferably a vinyl ester of a  $\text{C}_1$  to  $\text{C}_4$  alkanolic acid.

The self cross-linkable polymer typically contains 50-90% vinyl ester, 5 to 50% olefin, 0.5 to 10% cross-linking monomer and 0 to 10%

other, usually functional, monomers. A typical cross-linking monomer is N-methylol acrylamide although a wide range of other cross-linking monomers are available. The functional monomer may, for example, be acrylic acid.

Particularly preferred latices for use in the invention are Ethylene Vinyl Acetate (EVA) copolymers which optionally include at least one further monomer. Such further monomers may be used to modify the properties of the EVA polymer for use in a particular application, e.g. depending on whether a low stretch "hard" polymer system or high stretch "soft" polymer system is required. For example the ethylene and vinyl acetate may be copolymerised with at least one "hard" monomer such as styrene, methyl methacrylate or acrylonitrile, or with at least one "soft" monomer such as ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate or butadiene.

The ability to control stretch in this way is an important feature of the invention, particularly since stretch in the cross-direction of the paper (which usually extends around the circumference of the food product) may be controlled. This enables food casings of different stretch characteristics to be produced as required for different types of food product. In the prior art method of producing casing using viscose pre-treatment no such stretch control was available. Viscose pre-treatment produced a paper of limited stretch characteristics which could in general only be altered within limited bounds by the "draw" of the paper web through the impregnation and drying sections of the paper machine.

The latex will preferably comprise a dispersion of an Ethylene Vinyl Acetate copolymer (optionally including other monomers) cross-linked in an anionic stabilising system.

Typically latices are supplied with a solids content of 20-60% by weight. For use in the invention, such latices are preferably diluted to a solids content of less than 10% e.g. 4-6%.

A particularly suitable latex for use in the invention is Vinamul 3303. This is a self cross-linkable EVA latex which as supplied has a solids content of 50-54%, pH = 5.5, viscosity = 1.5 poise, and  $T_g = 0^\circ\text{C}$ . The Vinamul 3303 is preferably diluted to a solids content of 4-6% for use in this process.

A range of wet strength resins may be used. If however it is

intended that the final precursor material be subsequently treated with viscose to produce the finished food casing then the final wet strength system should be alkali resistant.

Suitable wet strength resins are water soluble cationic epichlorohydrin polyamide products, e.g. Kymene 709 as available from Hercules Ltd. which becomes alkali resistant in combination with the latex.

The amount of wet strength resin used in the coating composition will generally be less than 5% by weight of the composition. Best results are achieved using an amount of resin in the range 0.5-2.0% by weight.

If the latex used is one which would normally be, or tend to be, film forming then it will be necessary to include in the coating composition a small amount of a surfactant which will prevent the latex forming a film. The surfactant is preferably an anionic material, e.g. a higher alkyl sulphate (e.g. a dodecyl sulphate), a higher alkyl phenol polyether sulphate (e.g. nonylphenol polyether sulphate), a di-higher alkyl sulphosuccinate (e.g. sodium dioctyl sulphosuccinate), available under the trade name of "Alcopol O" from Allied Colloids), or a salt of a higher fatty acid (e.g. a stearate). The term "higher" in this context refers to aliphatic groups containing 8-22 carbon atoms.

The surface active agent also acts as an absorption aid to the absorption of the viscose coating during the "skin conversion" step thereby producing a better casing.

The amount of surface active agent used in the coating composition is preferably below 2% by weight. Use of higher amounts may reduce the wet/caustic strength of the precursor material. More preferably the amount of surface active agent present in the composition is less than 0.5% by weight, ideally less than 0.1% by weight.

If the surface active agent is used, it is highly preferred that the latex and surfactant are initially mixed together before addition and admixture of the wet strength resin to produce the final coating composition.

The coating composition preferably also includes a fibre consolidation aid usually in an amount less than 5% by weight of the



coating composition. More preferably the amount of fibre consolidation aid is less than 3% by weight of the coating composition. The fibre consolidation aid provides improved dry and wet tensile stretch in cross machine direction. Porosity can be controlled and caliper (thickness) is reduced producing a more consolidated sheet without a reduction of absorbency. This improves clarity of the finished casing and further improves the product's resistance to fracture lines. An enhancement of this clarity may be achieved by calendering.

Preferred examples of fibre consolidation aids which may be included are cellulose derivatives, e.g. alkyl cellulose derivatives, hydroxyalkyl cellulose derivatives, and (most preferably) carboxyalkyl cellulose derivatives. Particularly good results are obtained using carboxymethyl cellulose at a level of about 2% in the coating composition. The carboxymethyl cellulose also enhances the cross-linking of the wet strength resin.

Other fibre consolidation aids which can be used include galactomannans, for example guar gum and locust bean gum.

The coating composition may be applied to the porous substrate by any suitable technique, e.g. by spraying or by immersion of the material in the composition.

Typically an amount of coating composition of about 100-200% (e.g. 140-160%) of the weight of the porous substrate is applied thereto. If necessary, a size press or similar apparatus may be used to remove excess coating composition from the material so that only the desired amount of coating composition remains thereon.

In the next step of manufacture the material is dried, e.g. using steam heated drying cylinders. The treated material will preferably be dried to a total moisture content of less than 10% by weight more preferably less than 5% by weight.

Whilst we do not wish to be bound by any particular theory, we believe that during the drying step the latex is coagulated by removal of water to form a discontinuous coating on the fibres of the substrate. Since the composition is non-film forming, not all of the fibrous surface will be coated by the latex. Therefore these "uncoated" areas improve the absorption of viscose during final conversion of the precursor material to form the food casing.

In the next step the components of the coating are cross-linked.

This can be achieved by the following non-limiting examples. Raise web temperature to 100°C or above depending on available dwell time. The admixture can also be cross-linked by use of a suitable food grade initiator to catalyse the system, with a resultant reduction in web temperature and dwell time accordingly. During the cross-linking reaction, the polymer of the original latex cross-links with itself and the wet strength resin cross-links with itself, the polymer of the latex, and the fibres of the substrate.

The process in accordance with the invention for producing the food casing precursor material has a number of advantages as compared to the prior art processes in which viscose pre-treatment was used. More particularly, the process of the invention may be carried out with only a single impregnation or coating step (as compared to the 3-4 steps required for viscose pre-treatment) and the process does not have the disadvantages associated with viscose pre-treatment.

The invention will be illustrated by reference to the following non-limiting Examples.

#### Example 1

An abaca paper having a basis weight of about 18.5 gsm was size pressed with an aqueous solution containing

Diluted	<sup>1</sup> Vinamul 3303	providing	20% EVA
	<sup>2</sup> Kymene 709		2%
	<sup>3</sup> Alcopol		0.05%
	Water		Balance

<sup>1</sup> Cross-linkable EVA latex (ex Vinamul Ltd.)

<sup>2</sup> Polyamide/epichlorohydrin wet strength resin (ex Hercules)

<sup>3</sup> Surfactant based on sodium dialkyl sulphosuccinate (ex Allied

Colloids).

The size pressing was effected so that the paper was impregnated with its own weight of the coating composition.

The web was dried utilizing a Kodak glazing cylinder and the system cross linked by Hedinair hot air oven. The physical properties (A) of the web are listed in Table 1.

#### Example 2

An abaca paper having a basis weight of about 20.23 gsm was treated as in Example 1 except that the amount of the vinylacetate ethylene polymer in the coating composition was reduced to 15% by weight. The polyamide epichlorohydrin resin (Kymene 709) was reduced to 1.5% by weight while the surface active agent (Alcopol) was kept at 0.05%. The web was dried utilizing a Kodak glazing cylinder and the system cross linked by Hedinair hot air oven. The physical properties (B) are set forth in Table 1.

#### Example 3

The procedure of Example 1 was repeated using an abaca paper having a basis weight of about 21.2 gsm. The amount of vinylacetate ethylene polymer in the coating composition was reduced to 7.5% by weight and the polyamide epichlorohydrin resin reduced to 0.9%, while the surface active agent was retained at 0.05% by weight. The properties of the bonded web (C) are set forth together with the properties of a viscose bonded material (D) in Table 1.

#### Example 4

A casing made from the new binder system was compared to casing made from a viscose binder system but typically showed the new binder to be equivalent to viscose pre binder in its effect on the finished casing product. The properties of the finished casing are set forth in Table 2.

TABLE 1

PROPERTY	UNITS	A	B	C	D
BASIS WEIGHT	gsm	22.8	23.8	23.1	22.1
POROSITY	m <sup>3</sup> /min/m <sup>2</sup>	109.4	118.9	100.0	115.0
DRY TENSILE	MD g/25mm	4200	3938	3900	4100
DRY TENSILE	CD g/25mm	2875	2901	2900	2750
RATIO		1.5	1.4	1.3	1.5
DRY STRETCH	MD %	2.2	2.8	1.9	1.8
DRY STRETCH	CD %	8.2	7.3	5.2	5.9
WET TENSILE	MC g/25mm	1500	1300	1350	1125
WET TENSILE	CD g/25mm	1125	976	1000	837
WET GRAIN RATIO		75.0	75.0	74.0	74.7
WET STRETCH	MD %	8.4	7.2	6.4	5.8
WET STRETCH	CD %	11.5	10.2	8.3	7.9
CAUSTIC TENSILE	MD g/25mm	910	625	375	275
CAUSTIC TENSILE	CD g/25mm	840	500	300	175
VISCOSE ABSORBENCY	mm	109.0	103.0	93.0	95

TABLE 1 KEY

A:-	20%	Vinamul 3303 EVA	(1)
	2%	Hercules 709 Kymene	(2)
	0.05%	Allied Colloids "O" Alcopol	(3)
	77.95%	Water	
B:-	15%		(1)
	1.5%		(2)
	0.05%		(3)
	83.5%		(4)
C:-	7.5%		(1)
	0.9%		(2)
	0.05%		(3)
	91.6%		(4)
D:-	3.0%	Viscose solution	

TABLE 2

PROPERTY	UNIT						
PRE BINDER	TYPE	LATEX	LATEX	LATEX	VISCOSE	VISCOSE	VISCOSE
SKIN WT	gsm	91.0	86.0	112.0	91.0	86.0	112.0
BASE WEB WT	gsm	19.0	21.0	24.0	19.0	21.0	24.0
DRY TENSILE MD	g/25mm	11125	10205	13242	11222	10432	13132
DRY TENSILE CD	g/25mm	10200	9852	8115	9325	10372	14057
RATIO		1.09	1.04	1.63	1.20	1.01	0.98
DRY STRETCH MD	%	10.41	11.80	11.87	11.16	8.05	9.04
DRY STRETCH CD	%	31.87	30.95	35.87	24.79	22.24	26.90
WET TENSILE MD	g/25mm	6690	6310	7360	6017	6690	8912
WET TENSILE CD	g/25mm	5942	6260	4500	5137	6652	8242
WET STRETCH MD	%	18.83	15.65	16.79	15.51	16.84	19.47
WET STRETCH CD	%	22.47	22.08	30.23	19.10	22.02	22.66

TABLE 2 KEY

Latex Binder System - Product C from Table 1.

Viscose Binder System - Product D from Table 1.

CLAIMS

1. A porous bonded fibrous sheet material comprising a porous fibrous substrate and a bonding system which is the product obtained by cross-linking a non-film forming coating composition containing a polymer latex and a wet-strength resin.

2. A material as claimed in Claim 1 wherein the porous substrate is a wet laid substrate.

3. A material as claimed in Claim 2 wherein the wet laid substrate is a paper.

4. A material as claimed in any one of Claims 1 to 3 wherein the amount of the cross-linked composition is less than 40% by weight of the uncoated substrate.

5. A material as claimed in Claim 4 wherein the amount of the cross-linked composition is less than 20% by weight of the uncoated substrate.

6. A method of producing a porous bonded fibrous sheet material comprising treating a porous fibrous substrate with a coating composition which under the conditions of the treatment does not form a film and which is an admixture of a polymer latex and a wet strength resin, and effecting cross-linking of the polymer and resin applied to the substrate to produce a porous bonded fibrous sheet material.

7. A method as claimed in Claim 6 wherein the fibrous substrate is a wet laid substrate.

8. A method as claimed in Claim 7 wherein the wet laid substrate is a paper.

9. A method as claimed in any one of Claims 6 to 8 wherein the latex is a dispersion of a polymer which is self cross-linkable.

10. A method as claimed in any one of Claims 6 to 9 wherein the latex is a dispersion of a copolymer of an olefin and an unsaturated ester.

11. A method as claimed in Claim 10 wherein the latex is a dispersion of a copolymer of ethylene and vinyl acetate.

12. A method as claimed in any one of Claims 6 to 12 wherein the coating composition contains less than 10% by weight of the latex polymer.

13. A method as claimed in Claim 13 wherein the coating composition contains 4-6% of the latex polymer.

14. A method as claimed in any one of Claim 6 to 14 wherein the wet strength resin is present in the coating composition in an amount of less than 5% by weight.

15. A method as claimed in Claim 15 wherein the wet strength resin is present in the coating composition in an amount of 0.5-2.0% by weight.

16. A method as claimed in any one of claims 6 to 15 wherein the wet strength resin is a water soluble cationic epichlorohydrin polyamide product.

17. A method as claimed in any one of Claims 6 to 16 wherein the coating composition additionally comprises a surface active agent.

18. A method as claimed in Claim 17 wherein the surface active agent is an anionic material.

19. A method as claimed in Claim 18 wherein the surface active agent is a higher alkyl sulphate, a higher alkyl benzene sulphonate, a higher alkyl phenol polyether sulphate, a di-higher alkyl sulphosuccinate or a salt of a higher fatty acid.

20. A method as claimed in any one of Claims 17 to 19 wherein the surface active agent is present in the coating composition in an amount below 2% by weight.

21. A method as claimed in Claim 20 wherein the surface active agent is present in the coating composition in an amount less than 0.5% by weight.

22. A method as claimed in Claim 21 wherein the surface active agent is present in the coating composition in an amount less than 0.1% by weight.

23. A method as claimed in any one of claims 6 to 22 wherein the coating composition additionally comprises a fibre consolidation aid.

24. A method as claimed in claim 23 wherein the fibre consolidation aid is present in an amount less than 5% by weight.

25. A method as claimed in claim 23 or 24 wherein the fibre consolidation aid is a cellulose derivative.

26. A method as claimed in claim 25 wherein the cellulose derivative is carboxymethyl cellulose.

27. A method as claimed in claim 23 or 24 wherein the fibre consolidation aid is a galactomannan.

28. A method as claimed in claim 27 wherein the galactomannan is guar or locust bean gum.

29. A method as claimed in any one of Claims 6 to 28 wherein the coating composition is applied in an amount of 100-200% by weight of the porous substrate.

30. A method as claimed in any one of Claims 6 to 29 wherein the coated substrate is dried prior to the cross-linking reaction.



31. A method as claimed in Claim 30 wherein the drying is effected to a total moisture content of less than 10% by weight.

32. A method as claimed in Claim 31 wherein the coated material is dried to a moisture content of less than 5% by weight.

33. A method as claimed in any one of Claims 6 to 32 wherein the cross-linking is effected at a temperature of at least 100°C.

34. A food casing material which comprises the bonded sheet material as claimed in any one of Claims 1 to 5 or as produced by the method of any one of Claims 6 to 32 treated with viscose.

35. A food product (e.g. a meat product such as a sausage or salami) enclosed within a food casing material as claimed in Claim 34.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 94/02211

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A22C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A, 0 459 040 (THE DEXTER CORPORATION) 4 December 1991 see page 4, line 9 - line 45; claims 1-22	1
A	EP, A, 0 531 097 (THE DEXTER CORPORATION) 10 March 1993 see page 5, line 14 - page 7, line 25; claims 1-20	1
A	EP, A, 0 453 925 (HOECHST AG) 30 October 1991 see claims 1-9	1
A	FR, A, 2 355 954 (C.H. DEXTER LTD.) 20 January 1978 see page 8, line 33 - page 10, line 39; claims 1-30	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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